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Effect of doping of molybdenum on the optical properties of glasses of the As—S system

P. S. Provotorov[✉1], V. T. Avanesyan[1], M. Krbal[2], A. V. Kolobov[1]

[1] Herzen State Pedagogical University of Russia, 48 Moika Emb., Saint Petersburg 191186, Russia
[2] Center of Materials and Nanotechnologies, University of Pardubice,
95 Studentská, 532 10 Pardubice 2, Czech Republic

Authors

Pavel S. Provotorov, ORCID: 0000-0003-1117-5431, e-mail: p.provotorov95@yandex.ru

Vachagan T. Avanesyan, ORCID: 0000-0001-5772-8375, e-mail: avanesyan@mail.ru

Milos Krbal, ORCID: 0000-0002-8317-924X

Alexander V. Kolobov, ORCID: 0000-0002-8125-1172

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Abstract. This article discusses the spectral dependences of the absorption coefficient of thin arsenic sulphide films obtained by spin-coating, identified using a single-beam spectrophotometer in the wavelength range of 400–1000 nm. The effect of doping of molybdenum on the optical band gap is studied. While for a pure glass the band gap decreases with higher sulphur concentration, the opposite trend is observed in glass doped with molybdenum. Molybdenum doping also leads to an increase in Urbach energy. The obtained experimental curves are compared with theoretical ab-initio calculations.

Keywords: arsenic sulfide, molybdenum, spin-coating, optical band gap, Urbach energy.

Introduction

Glasses containing sulphur (S), selenium (Se) or tellurium (Te) are known as chalcogenide glassy semiconductors (ChGS). One of the features of ChGS is their ability to change properties under the influence of external factors (Kolobov 2006). In particular, this is due to the fact that in ChGS, along with the valence electrons involved in the formation of the covalent bond, there are pairs of electrons—the so-called lone electron pairs (LP-electrons)—the electronic states of which are located at the top of the valence band. This determines their response to the electronic excitation of the system (Kastner et al. 1976). Currently, these glasses are widely used in devices of infrared and integral optics, optical imaging and optical data processing due to their unique properties. The creation of stable and durable glasses with certain optical and electrical properties is an important goal for the physics of condensed state. Structural modification by varying the composition of a material is one of the ways to achieve this.

In practice, either binary compounds (Ge—Te, Sb—Te) or multicomponent ChGS systems such as (As—Se—S, Ge—As—S) are used. One of the most studied is the compound of arsenic sulphide As—S. It can be assumed that modifying this composition by molybdenum makes it is possible to vary its structural features. Since the atoms of transition metals have six-fold coordination, the bonds are formed with empty *d*-orbitals of the metal and LP-electrons of chalcogenides. These are the so-called donor-acceptor bonds. As a consequence, the concentration of inert LP electrons in such materials decreases (Kolobov et al. 2020).

In this paper, we studied the optical characteristics of thin film of $As_xS_{(100-x)}$ (x = 15–40) composition, as well as the impact of the transition metal molybdenum on the optical properties. The choice of molybdenum is due to the fact that molybdenum disulphide MoS_2 is one of the most studied materials at present, and it is of interest to study the effects of doping of molybdenum on a typical sulphur-based ChGS. The paper also compares experimental data and the results of ab-initio modelling.

Experimental methods

Thin films with and without a transition metal: $As_xS_{(100-x)}$ and $As_xS_{(100-x)}$: Mo (x = 15–40) as samples. The films were obtained by spin-coating on a glass substrate. The thickness of the films was ~300 nm. The advantages of this method are as follows: the possibility to obtain uniform films over large areas of a given thickness and composition close to stoichiometric, at a low cost of equipment (Krbal et al. 2007). The doping of arsenic sulphide with a transition metal was carried out by adding a $(NH_4)_2MoS_4$ dissolved in propylamine. This solution was mixed with As—S solutions. The study of the morphology and composition of the films under consideration was carried out using a scanning electron microscope (SEM).

Transmission and reflection spectra were measured using a single-beam spectrophotometer SF-2000 in the wavelength range λ = 400–1000 nm in 1 nm increments.

Ab-initio simulations were performed using the CASTEP software (Clark et al. 2005).

Results and discussion

Figures 1 and 2 show the spectrophotometry results of the thin films of arsenic sulphide $As_xS_{(100-x)}$ and those containing molybdenum Mo, respectively. Three notable regions can be identified in the transmission spectra: strong absorption in the region of short wavelengths, transparency in the long-wavelength region and—between them—the fundamental absorption edge. The obtained high transmittance region (~70–80%) spectra have an oscillatory character, due to the presence of light interference in the film-substrate system.

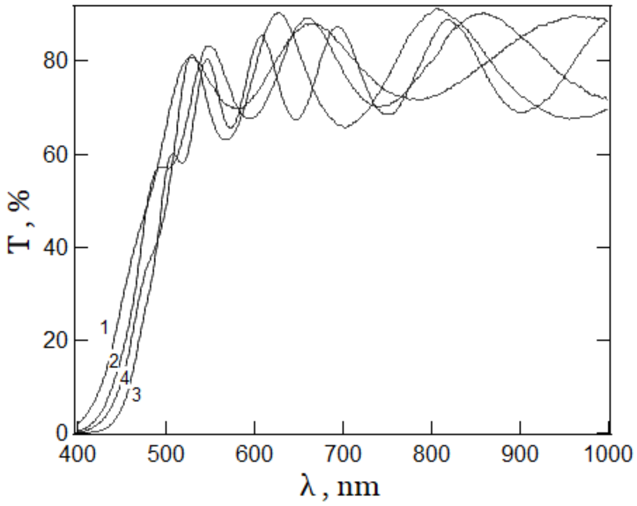

Fig. 1. Transmission spectra of As—S chalcogenide films with compositions:
$As_{15}S_{85}$ (1), $As_{20}S_{80}$(2) $As_{30}S_{70}$(3) $As_{33}S_{67}$(4)

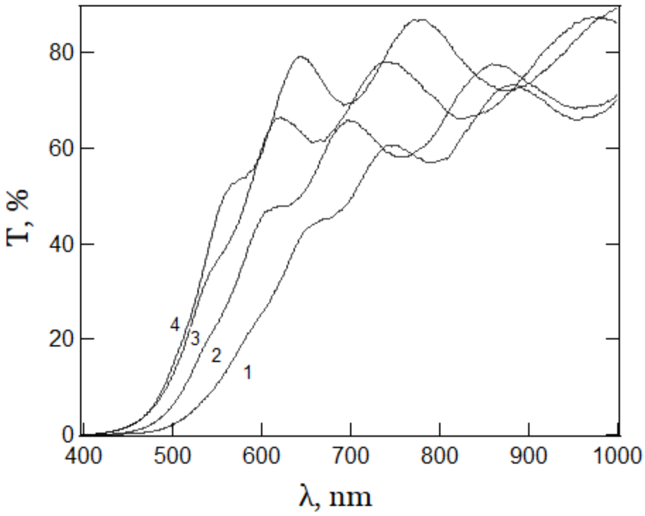

Fig. 2. Transmission spectra of As—S:Mo chalcogenide films with compositions: $As_{25}S_{75}$ (1), $As_{30}S_{70}$(2) $As_{33}S_{67}$(3) $As_{40}S_{60}$(4)

It is interesting to note that with an increase in sulphur concentration in the As—S system, the fundamental absorption edge shifts towards longer waves; however, in the presence of a transition metal in the film, the shift occurs towards shorter wavelengths.

In the region of strong absorption, for the dominant indirect allowed optical transitions characteristic of arsenic sulphide, the optical band gap E_{gopt} is related to the absorption coefficient α by Tauc extrapolation (Tauc et al. 1966):

$$\alpha h\nu = A\,(h\nu - E_g)^2, \qquad (1)$$

where, A is a constant depending on the nature of optical transitions. Previously, this approach has been successfully used in particular in (Lazarenko et al. 2019) to study a compound of Ge—Sb—Te system.

The dependences of the expression $(\alpha h\nu)^{1/2}$ on the photon energy (Figures 3; 4) are characterized by linearity in the region of strong absorption ($\alpha \sim 10^4$ см$^{-1}$). Extrapolation of the tangent in this area to the intersection with the horizontal axis allowed us to determine the values of the optical band gap E_{gopt} (Table 1). The table demonstrates that, in an arsenic sulphide film without a transition metal, the band gap decreases with increasing sulphur content, while in the composition with molybdenum, the gap increases when the concentration of sulphur is increased. It is also seen that doping of a transition metal significantly reduces the band gap.

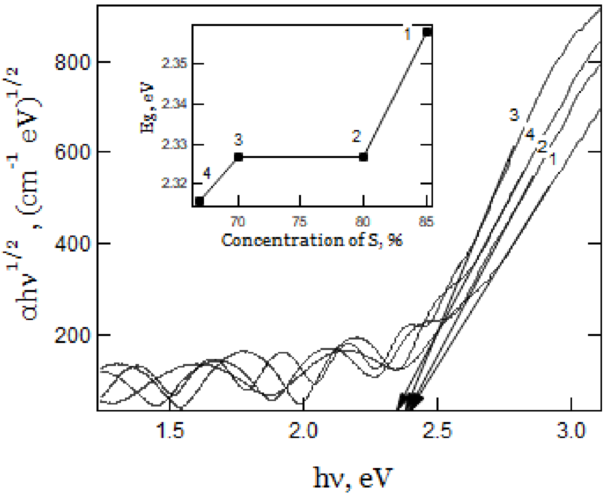

Fig. 3. Dependence of $(\alpha h\nu)^{1/2}$ on photon energy $h\nu$ in chalcogenide glasses As—S with composition: $As_{15}S_{85}$ (1), $As_{20}S_{80}$(2) $As_{30}S_{70}$(3) $As_{33}S_{67}$(4) from which the optical gap E_{gopt} is determined

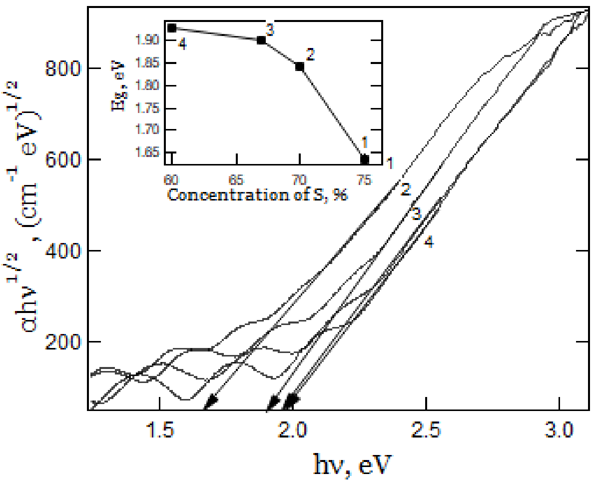

Fig. 4. Dependence of $(\alpha h\nu)^{1/2}$ on photon energy $h\nu$ in chalcogenide glasses As—S:Mo with composition: $As_{25}S_{75}$ (1), $As_{30}S_{70}$(2) $As_{33}S_{67}$(3) $As_{40}S_{60}$(4) from which the optical gap E_{gopt} is determined

Table 1. Optical parameters

Film composition	Optical band gap As—S, E_{gopt}, eV	Optical band gap As—S: Mo, E_{gopt}, eV	Urbach energy As—S, E_u, eV	Urbach energy As—S: Mo, E_u, eV
$As_{15}S_{85}$	2.3579	–	0.121	–
$As_{20}S_{80}$	2.3268	–	0.143	–
$As_{25}S_{75}$	–	1.6346	–	0.249
$As_{30}S_{70}$	2.3266	1.8422	0.122	0.143
$As_{33}S_{67}$	2.3158	1.9009	0.077	0.19
$As_{40}S_{60}$	–	1.9293	–	0.21

For glassy compounds, an exponential change in the absorption coefficient is often observed around the absorption edge. This dependence is often called an Urbach edge (Urbach 1953), and is described by the expression:

$$\alpha(h\nu) = \alpha_o \exp - [(E_{gopt} - h\nu) / E_U)], \qquad (2)$$

where E_U is the characteristic Urbach energy corresponding to the depth of penetration of the “tail” of localized states into the forbidden band.

The values of Urbach energy calculated from the slope of the linear section of the dependence ln (α) on the photon energy (Fig. 5; 6) for the samples under consideration are presented in Table 1. The obtained values of Urbach energy are higher than typical (Mott, Davis 1979) by the order of ~0.05 eV. We believe that this may be due to the technology we used to obtain samples and the presence of uncontrolled residues of solvents.

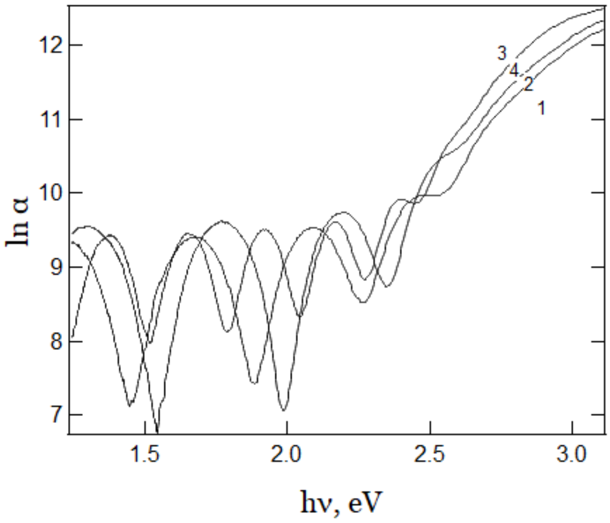

Fig. 5. The dependence of the absorption coefficient logarithm (ln α) on the photon energy *hν* in chalcogenide glasses As-S of composition: $As_{15}S_{85}$ (1), $As_{20}S_{80}$(2) $As_{30}S_{70}$(3) $As_{33}S_{67}$(4) from which the Urbach energy E_U is determined.

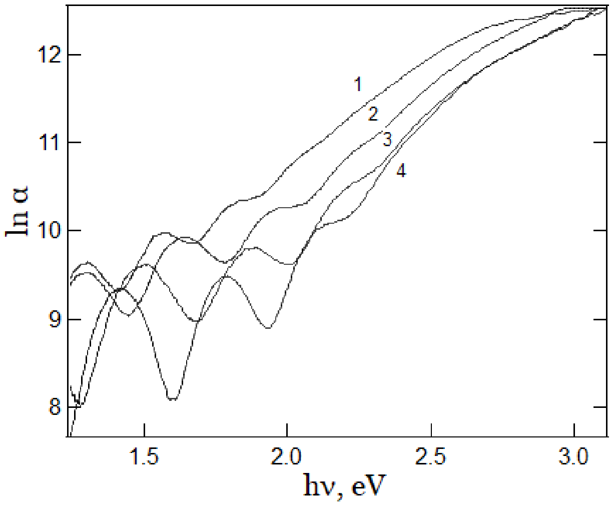

Fig. 6. Dependence of the logarithm of the absorption coefficient (ln α) on the photon energy *hν* in chalcogenide glasses As—S of composition: $As_{25}S_{75}$ (1), $As_{30}S_{70}$(2) $As_{33}S_{67}$(3) $As_{40}S_{60}$(4) from which the Urbach energy E_U is determined.

In parallel with the experimental study, the optical parameters of amorphous As_2S_3 (with and without molybdenum) were calculated in an ab-initio simulation based on the density functional theory. Figure 7 shows the calculated spectral dependences of the absorption coefficient. Note the absorption spectrum of As_2S_3 doped with molybdenum is shifted towards lower energies, which corresponds to a decrease in the band gap upon doping and is in agreement with experiment. The calculated value of the band gap is less than the corresponding experimental values, which is a well-known feature of such DFT calculations (Perdew 1985).

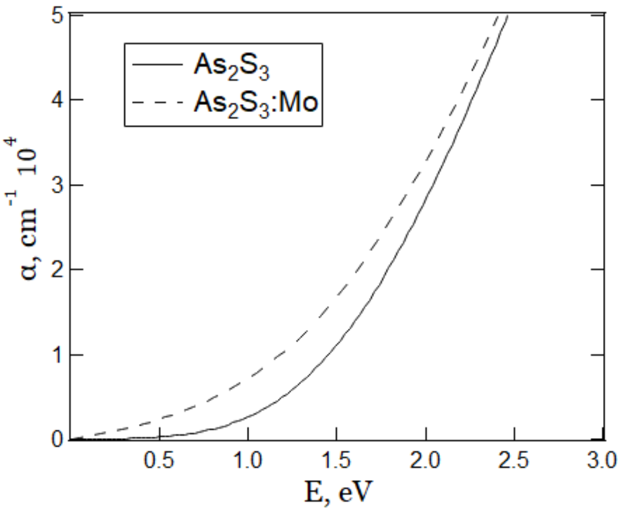

Fig. 7. Spectral dependence of the absorption coefficient obtained by DFT calculation

Conclusion

Thus, the study of the spectral dependences of the absorption coefficient of thin glassy films of the As—S system obtained by the spin-coating method made it possible to determine the values of the optical band gap, which correlate with the results of studies of films obtained by different methods (Němec et al. 2005; Yamaguchi 1985). It was shown that doping of the transition metal leads to a significant decrease in the band gap, as well as to the inversion of the compositional dependence of the band gap. Specifically, in a pure sample the optical gap increased with an increase in the ratio of sulphur in the composition, in samples containing molybdenum it decreased with an increase in sulphur. The experimentally observed decrease in the band gap with the introduction of molybdenum is confirmed by calculations from ab-initio.

Author contributions

Provotorov—conducting experiments, writing the article, Avanesyan—discussion of results, Krbal—making samples, Kolobov—performing DFT calculations, writing the article.

All authors discussed the final work.

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